Photochemistry of Some Benzopyrazinobarrelenes†

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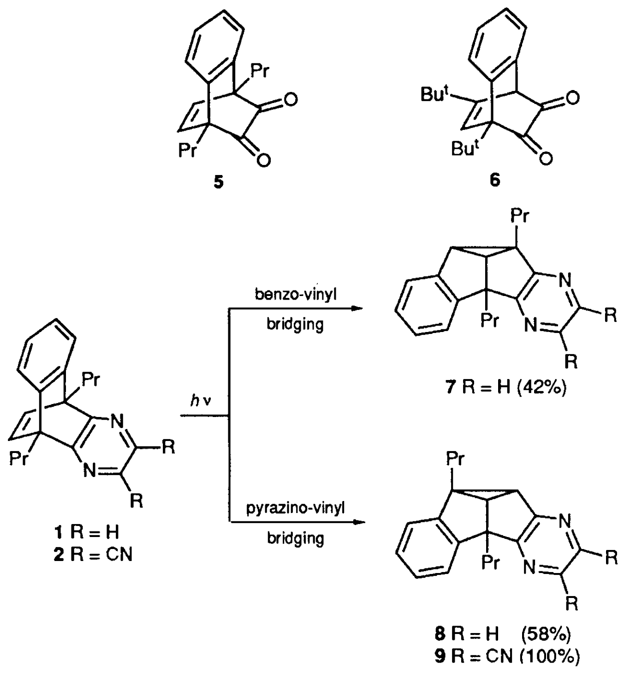
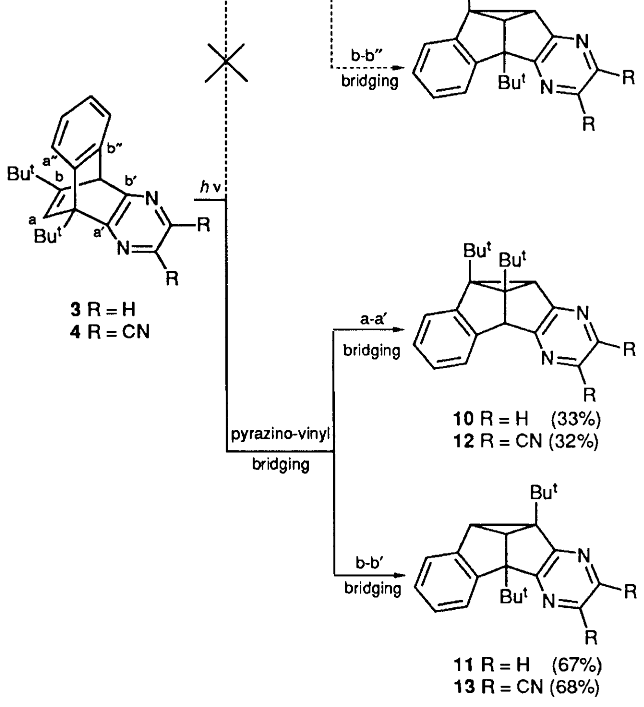
The photorearrangements of the benzopyrazinobarrelenes **1–4** to give benzopyrazinosemibullvalenes have been studied in order to examine the competing aptitude of benzene and pyrazine intramolecularly.

We have recently reported the photochemistry of some pyrazinobarrelenes[1] that showed similarities with and differences from that of benzobarrelenes;[2] the di-π-methane rearrangement occurred in both the direct irradiation and the sensitization reactions in the case of pyrazinobarrelenes, and the extent of pyrazino–vinyl bridging increased in comparison with benzo–vinyl bridging. The photochemical behaviour of benzopyrazinobarrelenes **1–4** would be interesting because the benzene and pyrazine moieties may compete intramolecularly. We report herein our findings.



Scheme 1

Benzopyrazinobarrelenes **1** and **3** were prepared from condensation of α-diketones **5**[3] and **6**[4] with ethylenediamine followed by oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), in 56 and 50% yields respectively, whereas **2** and **4** were synthesized from condensation of **5** and **6** with



Scheme 2

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† Benzopyrazinobarrelene = 5,8-dihydro-5,8-ethenobenzo[*g*]quinoxaline; benzopyrazinosemibullvalene = 10,11-dihydro-5,10,11-metheno-5*H*-benzo[4,5]cyclohepta[1,2-*b*]pyrazine.

1,2-diamino-1,2-dicyanoethylene in 41 and 26% yields respectively.

Irradiation of **1** in benzene with light of 350 nm in a Rayonet reactor afforded the benzopyrazinosemibullvalenes **7** and **8** in 42 and 58% yields *via* benzo–vinyl and pyrazino–vinyl bridging respectively, whereas only pyrazino–vinyl bridging occurred to give **9** in the case of **2** (Scheme 1). In contrast, irradiation of **3** and **4** yielded only pyrazino–vinyl bridging products **10** (33%) as well as **11** (67%), and **12** (32%) as well as **13** (68%) respectively (Scheme 2); **10** and **12** were formed *via* a–a′ bridging whereas **11** and **13** were produced *via* b–b′ bridging. The gross structures of **7–13** were determined from their spectroscopic properties, mainly their ^{1}H and ^{13}C NMR spectra.‡ The regiochemistry of the propyl groups and *tert*-butyl groups was established by ^{13}C spectroscopy (1D) with selective ^{1}H decoupling, COSY, and INADEQUATE; details will be published in a full paper.

The di-π-methane photorearrangement of benzopyrazinobarrelenes **1–4** may occur *via* a triplet state because both direct irradiation and sensitization with acetophenone as well as benzophenone gave the same products. Apparently intersystem crossing (isc) is very efficient in **1–4** because they possess a pyrazino moiety; the parent pyrazine[5] shows $\Phi_{\mathrm{isc}} = 1.0$. The preference for pyrazino–vinyl bridging over benzo–vinyl bridging may be due to the lower triplet energy of pyrazine [$E_{\mathrm{T}}(\mathrm{n},\pi^*)$ 75.9 kcal mol^{-1}; $E_{\mathrm{T}}(\pi,\pi^*)$ 80.0 kcal mol^{-1} (1 cal = 4.184 J)][6] in comparison with that of benzene (E_{T} 84.3 kcal mol^{-1})[7] and/or the stabilization effect of the nitrogen atoms.[1,8,9] However, it is not clear at present why only pyrazino–vinyl bridging occurs in the case of **3**. The cyano group greatly enhanced the pyrazino–vinyl bridging since **2** gave only **9**.[1]

There are two possible modes of pyrazino–vinyl bridging, a–a′ and b–b′; the latter predominates for **3** and **4**. It is interesting that a–a′ bridging is preferred in the case of a pyrazinobarrelene, 2,3-dicyano-5,8-dihydro-5,7,9-tri-*tert*-butyl-5,8-ethenoquinoxaline.[1]

The photochemistry of other heteroaromatic-fused barrelenes is currently under active investigation.

We acknowledge the National Science Council of the Republic of China for financial support of this work.

Received, 17th January 1991; Com. 1/00246E

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‡ *Spectroscopic data*, ^{1}H NMR in CDCl$_3$. **1**: δ 7.91 (s, 2H), 7.34–7.31 (m, 2H), 7.06–7.04 (m, 2H), 6.91 (s, 2H), 2.81–2.73 (m, 2H), 2.49–2.41 (m, 2H), 2.03–1.97 (m, 2H), 1.82–1.77 (m, 2H) and 1.26–1.23 (t, *J* 7.2 Hz, 6H). **3**: δ 7.97–7.96 (m, 1H), 7.85–7.81 (m, 2H), 7.36–7.33 (m, 1H), 7.05–6.97 (m, 2H), 6.41–6.40 (d, *J* 2.2 Hz, 1H), 5.10–5.09 (d, *J* 2.2 Hz, 1H), 2.01 (s, 3H), 1.59 (s, 3H), 1.53 (s, 3H) and 1.09 (s, 9H). **7**: δ 8.06–8.05 (d, *J* 3.0 Hz, 1H), 8.03–8.02 (d, *J* 3.0 Hz, 1H), 7.24–7.17 (m, 1H), 7.15–7.13 (m, 1H), 7.05–6.98 (m, 2H), 3.37 and 3.13 (AB, *J* 6.4 Hz, 2H), 2.44–2.37 (m, 2H), 2.29–2.22 (m, 1H), 1.75–1.67 (m, 1H), 1.61–1.53 (m, 2H), 1.44–1.35 (m, 2H), 1.02–0.98 (t, *J* 8.8 Hz, 3H) and 0.96–0.93 (t, *J* 7.4 Hz, 3H). **8**: δ 7.99–7.96 (m, 2H), 7.19–7.16 (m, 1H), 7.13–7.11 (m, 1H), 7.07–7.04 (m, 2H), 3.36 and 3.00 (AB, *J* 6.6 Hz, 2H), 2.42–2.29 (m, 3H), 1.72–1.64 (m, 1H), 1.56–1.48 (m, 2H), 1.42–1.36 (m, 2H), 1.01–0.97 (t, *J* 7.4 Hz, 3H) and 0.95–0.92 (t, *J* 7.2 Hz, 3H). **10**: δ 8.01–8.00 (d, *J* 3.0 Hz, 1H), 7.96–7.95 (d, *J* 3.0 Hz, 1H), 7.61–7.59 (m, 1H), 7.28–7.24 (m, 1H), 7.06–7.04 (m, 2H), 4.73 (s, 1H), 3.37 (s, 1H), 1.46 (s, 9H) and 1.15 (s, 9H). **11**: δ 8.07–8.05 (m, 2H), 7.54–7.51 (m, 1H), 7.20–7.17 (m, 1H), 7.01–6.99 (m, 2H), 3.38 and 3.35 (AB, *J* 6.8 Hz, 2H), 1.40 (s, 9H) and 1.17 (s, 9H).

^{13}C NMR in CDCl$_3$. **1**: δ 162.2 (s), 147.7 (s), 140.8 (d), 136.6 (d), 124.8 (d), 122.0 (d), 54.5 (s), 29.4 (t), 18.1 (t) and 15.2 (q). **3**: δ 161.8 (s), 161.7 (s), 161.2 (s), 147.3 (s), 145.2 (s), 136.4 (d), 136.3 (d), 129.5 (d), 125.6 (d), 124.6 (d), 124.4 (d), 124.1 (d), 61.6 (s), 54.1 (d), 34.9 (s), 33.5 (s), 29.1 (q), 28.6 (q), 27.7 (q) and 25.9 (q). **7**: δ 163.2 (s), 154.4 (s), 149.6 (s), 141.7 (d), 140.8 (d), 138.6 (s), 127.0 (d), 126.5 (d), 124.6 (d), 120.8 (d), 61.2 (s), 55.5 (d), 45.7 (s), 44.0 (d), 34.2 (t), 31.9 (t), 20.3 (t), 18.5 (t), 14.5 (q) and 14.2 (q). **8**: δ 164.1 (s), 154.3 (s), 149.1 (s), 141.5 (d), 140.5 (d), 139.2 (s), 127.2 (d), 126.9 (d), 124.2 (d), 120.8 (d), 61.4 (s), 55.4 (d), 49.6 (s), 40.6 (d), 35.3 (t), 31.9 (t), 20.2 (t), 18.5 (t), 14.5 (q) and 14.2 (q). **10**: δ 162.7 (s), 155.0 (s), 145.3 (s), 141.7 (d), 140.4 (d), 139.7 (s), 128.1 (d), 126.3 (d), 121.7 (d), 63.8 (s), 58.6 (d), 39.9 (d), 34.7 (s), 33.4 (s), 31.4 (q) and 31.0 (q). **11**: δ 163.3 (s), 154.0 (s), 149.1 (s), 140.8 (d), 140.4 (d), 140.3 (s), 126.7 (d), 126.3 (d), 124.8 (d), 123.7 (d), 68.0 (s), 51.6 (s), 50.8 (d), 38.8 (d), 35.4 (s), 32.6 (s), 27.9 (q) and 27.8 (q).